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To: Dr. D. Mills
Director of Research

**AN INVESTIGATION OF CANDIDATE FLUIDS FOR USE IN
HIGH TEMPERATURE HEAT PUMPS**

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A literature search for information concerning possible candidate working fluids for use in High Temperature Compression Heat Pumps (HTCHP) was conducted.

The information compiled indicates that there is no all-purpose working fluid which will satisfy all HTCHP applications. The effects of various lubricants, elastomers, and metals may also effect the stability of working fluids at the elevated temperatures which occur in HTCHP.

Currently, R114 is considered the best overall working fluid for use in HTCHP with condensing temperatures up to 120°C. The fluid R133a is thermodynamically comparable to R114, except availability and price deter its general acceptance. For condensing temperatures above 120°C, water is considered as the only candidate working fluid for use in HTCHP.

INTRODUCTION

In most cases, the fluids which are used in low or moderate temperature compression heat pumps cannot be used in HTCHP due to low critical temperatures or problems in stability. In this report, the basic classifications, desired properties, and various methods of testing candidate working fluids will be examined. Also included is a comparison, based on published experimental results, of some of the more promising working fluids to date.

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BASIC CLASSIFICATIONS FOR WORKING FLUIDS

Before a working fluid may be used in a vapour-compression heat pump, its associated thermodynamic properties must be known. Working fluids used in vapour-compression cycles are divided into two general categories according to how the fluid will behave when subjected to isentropic compression. Type "A" fluids (refer to Figure 1a) increase the amount of superheat when subjected to isentropic compression, while type "B" fluids (refer to Figure 1b) decrease the amount of superheat when subjected to isentropic compression.

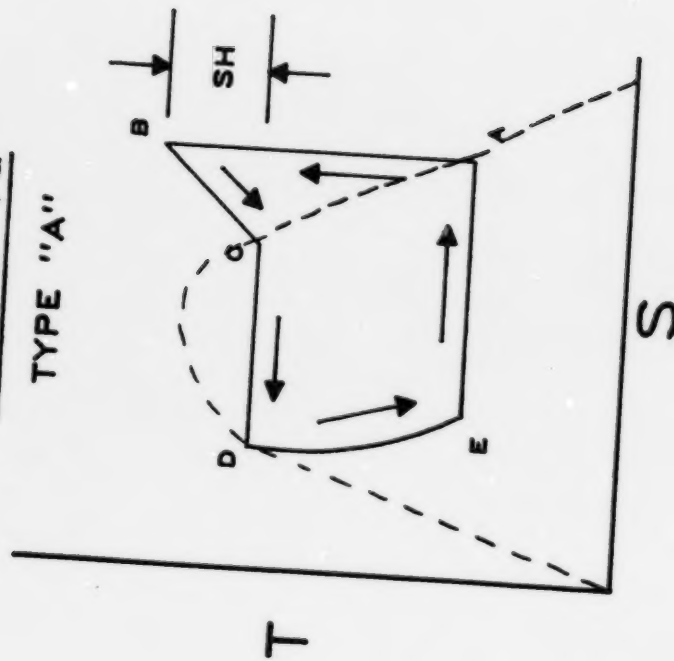
An example of the importance in this distinction can be shown by the following examples. To avoid vapour condensing during isentropic compression of a type "B" fluid, the fluid must be superheated prior to entering the compressor such that saturation conditions or hotter are encountered at the exit of the compressor. If a type "B" fluid is compressed without first being superheated, the vapour will begin to condense prior to exiting the compressor. Conversely, when a type "A" fluid is subjected to isentropic compression, the fluid will superheat during compression, and no condensation will occur. Therefore, knowledge of how the working fluid reacts to isentropic compression is of prime importance to the designer.

DESIRED PROPERTIES: WORKING FLUIDS AND LUBRICANTS

For a working fluid to be considered "ideal", it must pass certain thermodynamic and mechanical criteria. According to Taylor and Bertinat/1/, the qualities which an ideal working fluid must possess are as follows:

1. Critical temperature significantly higher than the highest temperature likely to occur in the system (condenser),
2. Normal boiling point significantly less than the lowest temperature in the system (evaporator),
3. A relatively high Coefficient of Performance (COP),
4. Relatively low Specific Compressor Displacement (SCD), which will ensure a high volumetric efficiency,
5. Saturation vapour pressure at highest design temperature must not be so high as to impose design limitations on the system,
6. Thermally stable at the highest temperatures likely to occur in the system,

FIGURE 1a
TYPE "A"



SH = AMOUNT OF SUPERHEAT

FIGURE 1b
TYPE "B"

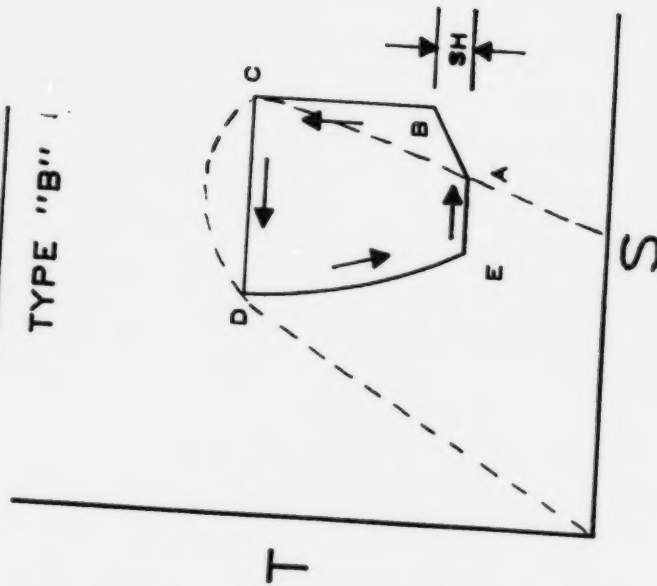


FIGURE 1

COMPARISON BETWEEN TYPE "A"(LEFT) AND
TYPE "B" (RIGHT) WORKING FLUIDS WHEN
SUBJECTED TO ISENTROPIC COMPRESSION

7. Chemically inert at the highest temperatures likely to occur in the system,
8. Non-toxic,
9. Non-flammable,
10. Readily available commercially,
11. Relatively inexpensive.

Unfortunately, there are no working fluids to date which fill all of the above criteria. Therefore, a trade-off must be made when selecting a working fluid to be used in a system. The advantages and disadvantages of candidate working fluids are discussed later.

Compressor lubricants also have a pronounced effect on the performance of some working fluids and vice versa. This modification of working fluid and lubricant properties is particularly noticeable at the elevated temperatures which occur in HTCHP. Also, some of the by-products which are produced by chemical interactions between lubricants and working fluids are acidic, and may lead to accelerated corrosion of system components. Therefore, knowledge of how various working fluid/lubricant combinations will react in a HTCHP becomes crucial prior to system development.

From Drakesmith/2/, the important characteristics of a lubricant are as follows:

1. Adequate viscosity
2. Inherent lubricity
3. Miscibility of work fluid
4. Range of viscosity grades
5. Acceptable cost
6. Adequate chemical stability

Due to constant exposure of the lubricants with the working fluid, the chemical behaviour of the mixture must be known.

FLUID TESTING

Preliminary testing of candidate working fluids prior to entering an actual system is of prime importance. Certain metals, ceramics, or elastomers may be affected by the presence of some working fluid/lubricant combinations, causing early deterioration of the heat pump system components. Therefore, prior testing of combinations of fluids, lubricants and construction materials is an essential step before a high temperature heat pump system may be designed.

There are basically two methods, static and cyclic, for testing the various combinations of working fluids, lubricants, metals, ceramics and elastomers. Each method has its own associated advantages and disadvantages which are discussed in the following two sections.

STATIC TESTING

Static testing provides essential data on the compatibility of working fluid/lubricant combinations through the use of accelerated testing. An excellent description of the procedure for Static testing of R114 may be found in the Sperry Research Report: "System Component Compatibility and R114 Stability"/3/. The test involved placing a measured amount of the candidate working fluid in glass tubes which had been previously sealed at one end. Combinations of various lubricants and or other test materials were then added to the glass tubes. The tubes were then evacuated, sealed and placed in a temperature controlled oven. Here the samples remained at constant temperature, somewhat greater than the fluid's maximum design temperature (eg, 204°C), for a predetermined length of time (eg, 15-90 days. After the oven test was completed, the samples were allowed to cool and then analyzed for percentage decomposition, acidity, corrosion rates, lubricant viscosity, etc.

Static testing provides a relatively quick and economical method for the analysis of large numbers of working fluid/lubricant combinations. However, static testing does not provide for an accurate simulation of the cycling effects which occur in an actual heat pump. For an improved simulation of an actual Compression Heat Pump (CHP) cycle, a cyclic test must be performed.

CYCLIC TESTING

Cyclic testing simulates the vapour-compression cycle which a fluid would be subjected to in an actual CHP. The working fluid is therefore in contact with the lubricant during all of its associated thermodynamic phases. There are a variety of methods currently in use for the cyclic testing of working fluids. Two examples are outlined in this section.

The "Fluid Decomposer" used by Drakesmith and Gibson/4/ at the Electricity Council Research Centre, Capenhurst England, provides an economical, compact and relatively quick means of determining the chemical effects of various working fluid/lubricant combinations. The "Fluid Decomposer" was designed to simulate the maximum chemical activity in a HTCHP, which was assumed to be located between the exhaust of the compressor and the inlet to the condenser. To simulate this, Drakesmith and Gibson decided that a steady flow of a working fluid/lubricant solution should be exposed to hot catalytic surfaces of copper, aluminum, and steel.

The operation of the "Fluid Decomposer" was as follows: Mixtures of working fluids and lubricants were circulated from a cooled sump, via a metering pump, and injected at 160° or 200°C into a copper tube containing an aluminum and steel spirally grooved core. Here the working fluid vapourized and continued up the tube to a condenser, where the working fluid was condensed prior to being returned to the sump. Meanwhile, the lubricant flowed downwards over the hot surface and returned to the sump ready to begin a new cycle. The various fluid/lubricant combinations were then ranked relative to their chemical behaviour (eg, percentage decomposition, build-up of decomposition products, and changes in physical properties of the working fluids and lubricants, etc.) during the tests. This is only one of the systems which has been developed at the Capenhurst facility. A schematic of the "Fluid Decomposer" has been included as Figure 2.

Another example of a cyclic fluid testing apparatus was the system used by the Thermo Electron Corporation, of Waltham, Massachusetts/5/. The system was used to test candidate working fluids for use in Rankine powered heat pumps, in connection with solar cooling. Figure 3 is a block diagram of the basic components used to test the stability of R11 and R113 in the presence of various lubricants. The apparatus was meant to simulate the effects of a Rankine power cycle on the combinations of working fluids and lubricants which were involved in the test. The pressure let down valve followed by a test section of pipe was used to simulate the effects of the working fluid/lubricant mixture on the materials which are used to construct turbine blades. Following the test period, the test section of pipe was removed and the lubricants, working fluids and materials were analyzed for peculiarities which evolved from any chemical reactions caused by the working fluid/lubricant combinations.

Both of the foregoing examples allow the working fluid/lubricant combinations to thoroughly mix during the various processes which

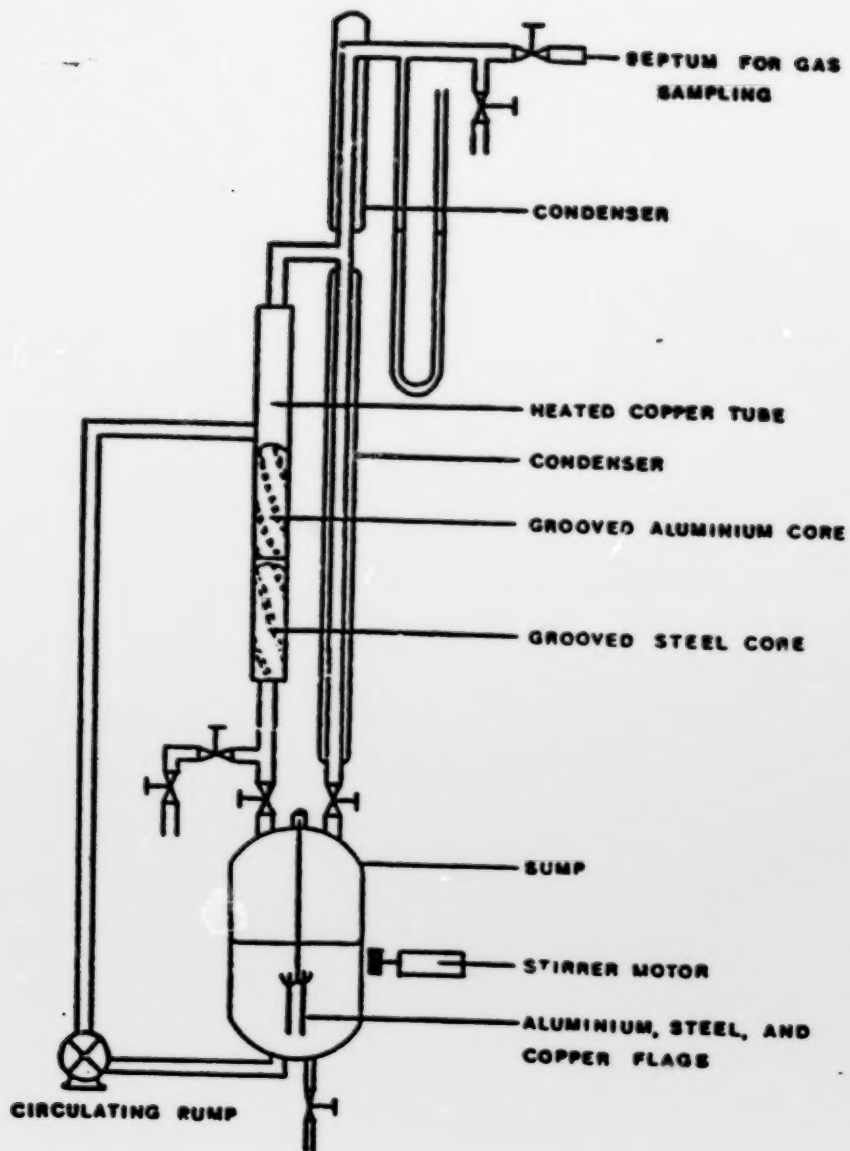


FIGURE 2: "FLUID DECOMPOSER" USED TO TEST STABILITY OF WORKING FLUID/LUBRICANT MIXTURES /4/

ALUMINUM TEST SECTION

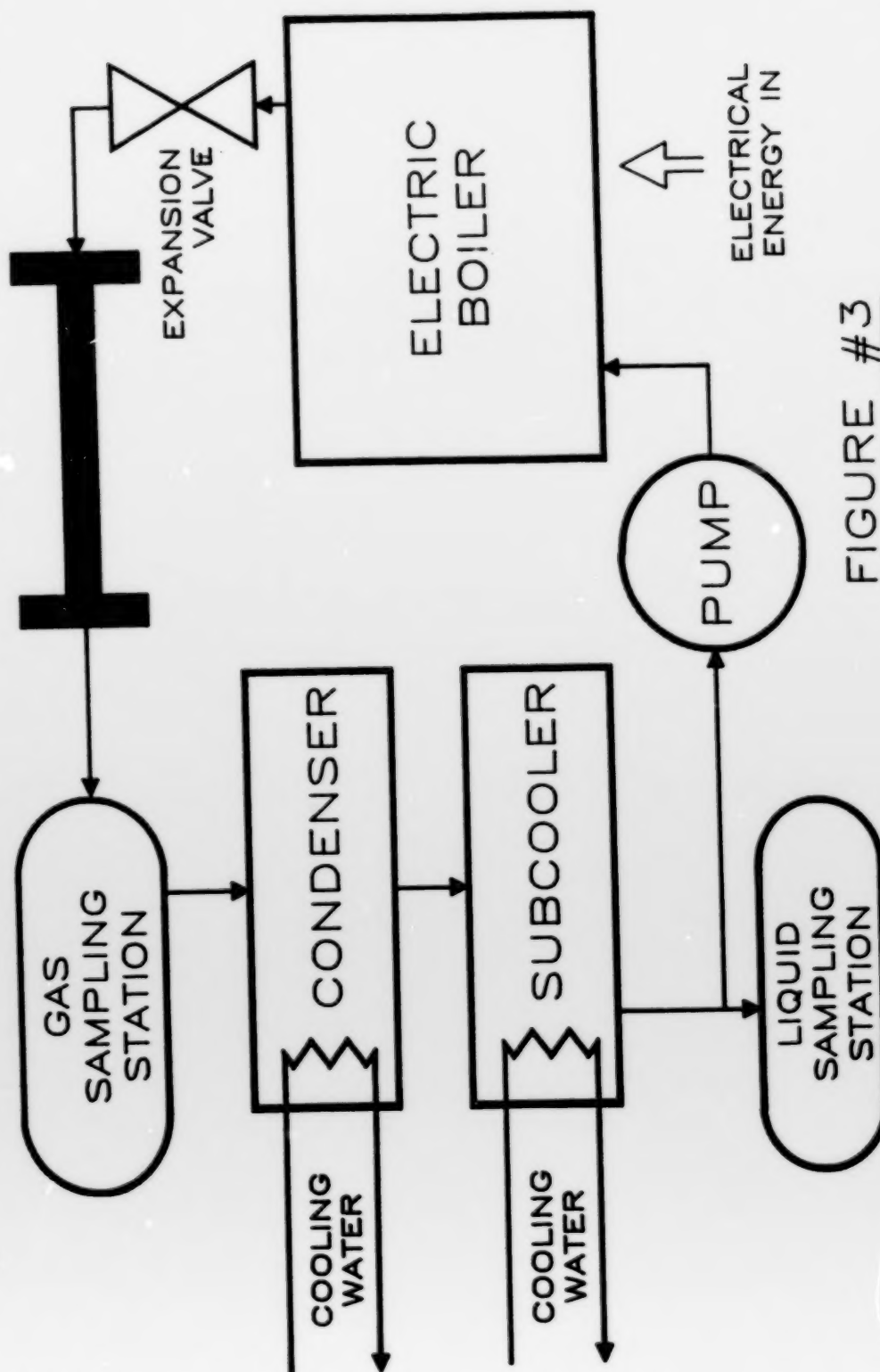


FIGURE #3

SIMPLIFIED TEST LOOP FOR
DETERMINING THE STABILITY OF R113 AND R111.[4]

occur during CHP or similar cycles. Cyclic testing produces excellent results, but substantially higher equipment costs and longer test periods are encountered for large numbers of working fluid/lubricant combinations. Therefore, static testing is preferred for large numbers of working fluid/lubricant combinations, and cyclic testing is preferred for specific combinations.

CANDIDATE WORKING FLUIDS FOR HTCHP

There are many fluids which are listed in the ASHRAE/6/ Handbook for use as working fluids for heat pumps. However, most of the working fluids generally found in lower temperature CHP's may be eliminated from consideration for use in HTCHP due to their critical temperatures, which are too low for use in HTCHP. This significantly reduces the available working fluids which can be used in HTCHP's, to a list of fluids which may be found in Table 1. The table outlines the various thermodynamic properties along with general comments on each of the fourteen fluids listed.

The list may be significantly reduced by considering some of the properties specified for an ideal working fluid, which were outlined earlier in this report. Fluorinal may be eliminated due to its high toxicity. The fluids R114B2 and R216 may be eliminated from the list since they are either difficult to obtain or are not commercially available. The working fluids 6FB and 5FB are undesirable since they are hazardous and expensive. PP1 was tested by Taylor and Bertinanti/1/ in a 150°C test HTCHP, and found to have a low COP (approximately 2.9) due to the fluid's poor thermodynamic properties and heat losses at the compressor. PP2 is regarded as yielding similar results as PP1, therefore, both are eliminated as possible candidates. The working fluid R21 was found to produce chemically corrosive by-products at the elevated temperatures which occur in HTCHP, and is therefore eliminated from further consideration.

This narrows the list to six possible candidate working fluids: R12B1, R11, R133a, R113, R114, and R718 (water). The selection from this list of working fluids for use in a HTCHP is primarily dependent on the type or presence of lubricants which the compressor requires, or on the maximum temperature of the system (condenser). For an example, R12B1, may not be used in the presence of mineral oil lubricants, due to the acceleration in the percentage decomposition of the fluid and the lubricant which results. The working fluid R11, which has a high critical temperature, is severely affected by the presence of lubricants at elevated temperatures, and is therefore only to be considered when a suitable "Dry" compressor is developed.

Table of Thermodynamic Data for Candidate Working Fluids Table 1

FLUID	MOL. WT.	Tcrit deg.C	Tbp deg.C	TYPE	Pcrit kPa	COMMENTS
FLOURINAL	99	227	74	A	X	Very toxic.
R114B2	260	214	47	B	X	Promising thermodynamic properties but may be chemically unstable at high temperatures. Toxic, and hard to obtain.
R216	221	180	36	B	2753	Unobtainable Commercially.
6FB	186	244	80	B	X	Anaesthetic and relatively expensive. Little thermodynamic data available.
5FB	168	230	85	B	X	Anaesthetic and relatively expensive. Little thermodynamic data available.
PP1	338	178	57	B	X	Non-toxic, good stability, poor thermodynamically relatively expensive. Little thermodynamic data available.
PP2	350	213	76	B	X	Same as PP1.
R21	103	178	9	A	5168	Chemically active at high temperatures when in the presence of lubricants. Corrosive at elevated temperatures.
R12B1	X	X	X	A	X	Doubtful stability, poor when in the presence of mineral lubricants at elevated temperatures.
* R11	137	198	24	A/B	4406	Highly unstable in the presence of lubricants at elevated temps. Good thermodynamic properties To be considered when a dry compressor developed.
* R133A	118	154	X	B	4050	Comparable to R114 thermodynamically, except has lower SCD resulting in higher volumetric eff. Toxic, slightly lower stability than R114.
* R113	187	214	47	B	3437	Good thermodynamic properties, but greatly effected by some lubricants at elevated temperatures.
* R114	171	146	3.8	B	3259	Considered by some to be the best fluid for use in HTWP in the range of 70 - 120 C. Low critical temperature but high stability.
* R718 (water)	18	374	100	A	22070	Good stability, best COP of all fluids. Worst SCD of all fluids requiring high volumetric flowrates. Considered only for VHTCNP's.

* Maybe Suitable for use in HTCNP

X Information Unavailable

CRITICAL TEMPERATURES AND BOILING POINTS FOR SELECTED FLUIDS

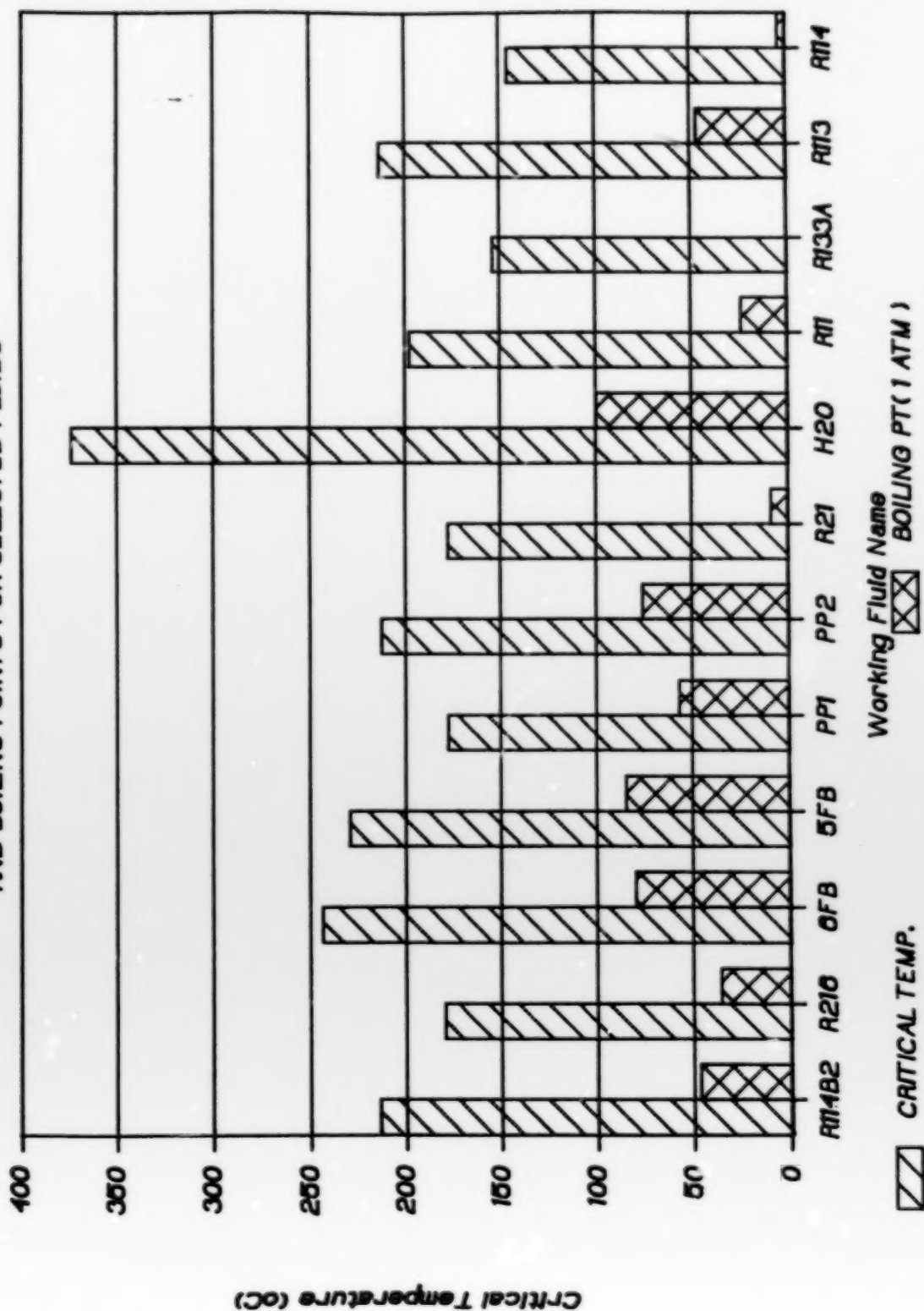


Figure 4

The working fluids R133a, R113, R114, and water have been tested with some synthetic lubricants, and found to be stable in HTCHP with condensing temperatures below 120°C. Each of these fluids are discussed below concerning their associated advantages and disadvantages.

The working fluid R133a (Chlorotrifluoroethane - $\text{CF}_3\text{CH}_2\text{Cl}$) is an intermediary of synthesis in organic chemistry, which until 1982 had not been used as a working fluid for HTCHP. The working fluid R133a was tested by Almin, Feuga, Vuillame/7/ of France. They tested R133a for 3000 hours in a laboratory heat pump with condensing temperatures between 70°C and 120°C. The lubricants used were RHONE 801 E23 oil and MOBIL OIL SHC 234 oil. The results indicated that R133a was an excellent refrigerant for HTCHP use, displaying good stability with the lubricants tested. Also, R133a is denser than R114 yielding a lower specific compressor capacity and hence higher volumetric efficiencies. This increase in volumetric efficiency means lower flowrates are required for the same heat transfer rates, and hence smaller compressors are required. However, R133a is currently more expensive than R114, due to limited production, which tends to penalize R133a for general acceptance as a HTCHP working fluid.

The working fluid R113 (Trichlorotrifluoroethane - $\text{CCl}_2\text{FCClF}_2$) has been well examined, documented and is currently used in Rankine powered heat pumps for the generation of process steam/8/. Thermodynamic properties for pure R113 are well known and documented in such publications as the ASHRAE Handbook; 1985 Fundamentals/6/ and in great detail in the research report; "Derived Thermodynamic Design Data for Heat Pump Systems Operating on R113"/9/.

The major disadvantage of R113 is that its chemical stability when in contact with lubricants is severely reduced. This fact has been mentioned in many articles/1,2,10,11/ as the major reason for neglecting R113 as a HTCHP working fluid. R113 has a higher critical temperature (as shown in Figure 4) than either R133a or R114, but the stability problems associated with R113 restrict the maximum operating temperature below that of both R133a and R114.

The working fluid R114 (Dichlorotetrafluoroethane - $\text{CClF}_2\text{CClF}_2$) is currently the third most commonly used propellant in aerosol applications/3/. Also, R114 has been used as a moderate temperature heat pump working fluid for quite some time, and is now being considered for use as a HTCHP working fluid.

In 1979, Ingvar A. Ekroth of The Royal Institute of Technology, Sweden, presented a report/11/ based on the thermodynamic evaluation of thirty candidate working fluids for use in three different vapour compressor cycles: Basic single stage cycle, a

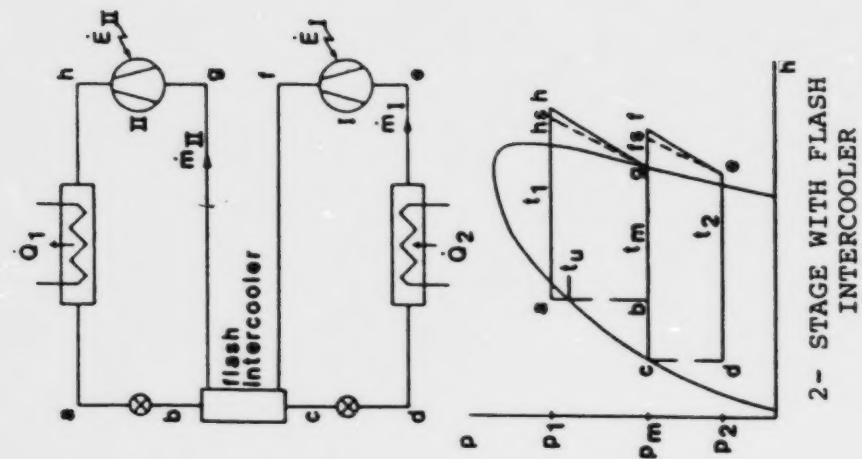
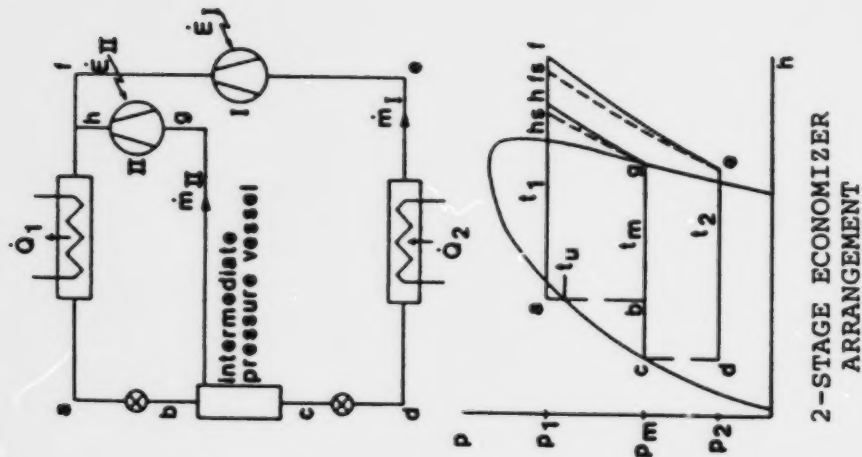
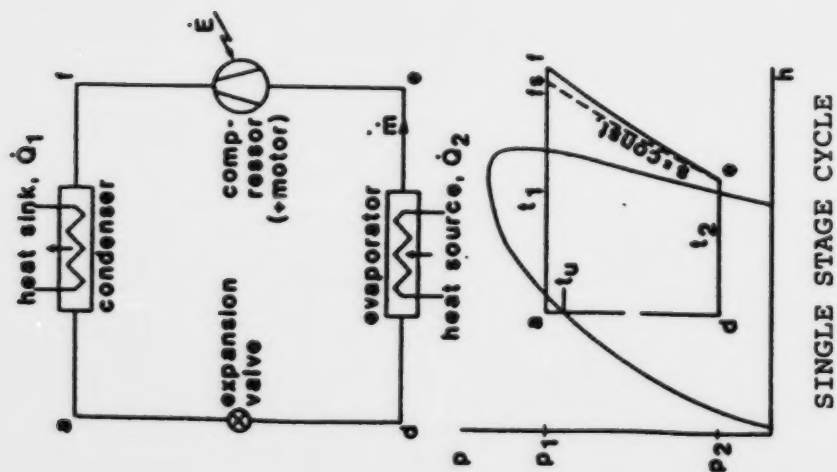


FIGURE 5: EQUIPMENT DIAGRAMS & SPECIFIC ENTHALPY VS PRESSURE DIAGRAMS FOR THREE CYCLES [10]

two stage cycle with economizer arrangement and a two-stage cycle with flash intercooling. (Refer to Figure 5 for equipment diagrams and Enthalpy - Pressure diagrams of the foregoing cycles.) The conclusion Ekroth made, based on: pressures, coefficients of performance, swept volumes, stability and availability, was that R114 was the best choice for a working fluid in HTCHP's with condensing temperatures between 100°C and 120°C. However, the analysis performed by Ekroth did not include specific fluid/lubricant combinations, meaning further investigations of specific working fluid/lubricant combinations were required.

The Sperry Research Centre released an extensive report in 1981 on the stability of R114 in the presence of various lubricants, metals and elastomer combinations/3/. The tests were performed at elevated temperatures using the static testing procedures, outlined in this report. Sperry concluded that the decomposition of R114 could be greatly influenced by the presence of some lubricants when steel surfaces were present to catalyze the reactions. Fluorocarbon and Silicone oils reacted very slowly with R114, while hydrocarbon oils caused extensive acceleration in the decomposition rate of R114 at temperatures as low as 177°C.

The test results from combinations of R114 and various elastomers were as follows. EPDM (Ethylene Propylene Diene terpolymer) and some Fluoroelastomers displayed sufficient resistance to decomposition in R114 to be considered for use as seals. However, all elastomers tested experienced considerable swelling in R114.

In 1982, a report by H. Bauder entitled "High Temperature Heat Pump Applications and Their Limitations"/12/ was published in the Sulzer Technical Review. Bauder concluded that for HTCHP with condensing temperatures below 130°C, the best working fluid based on: critical temperature, pressure at maximum system temperature (not to exceed mechanical structural constraints), chemical stability and lubricant compatibility was R114. Bauder also published a graph of the Performance ranges for the three major types of compressors used in HTCHP, namely: Turbocompressors, Screw Compressors and Piston Compressors, with R114 as the working fluid. This graph has been included as Figure 6.

Also in 1982, the International Research and Development Company (U.K.) presented a report on a prototype HTCHP, which was in the process of being developed/13/ (Refer to Figure 7 for a schematic of the prototype system). The prototype HTCHP was to be used in the production of process steam utilizing a reciprocating gas engine in connection with a piston compressor. An analysis of candidate working fluids, included in the report, resulted in the selection of R114 as the best working fluid.

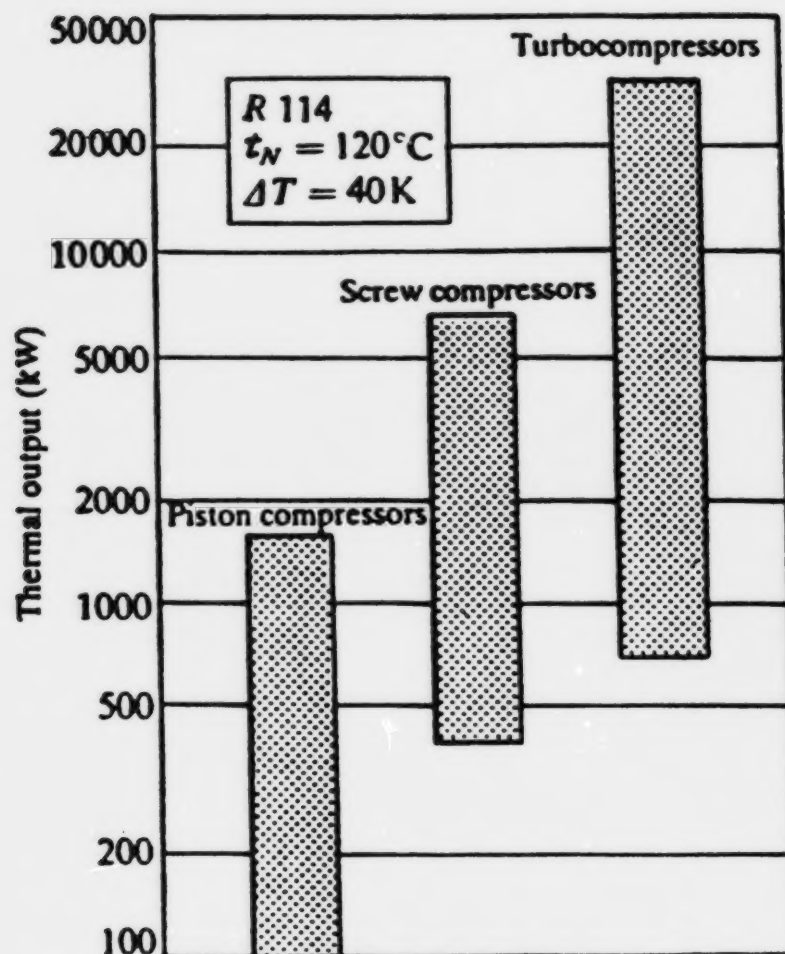


FIGURE 6: OPERATING RANGES FOR THREE TYPES OF COMPRESSORS OPERATING WITH R114/11/

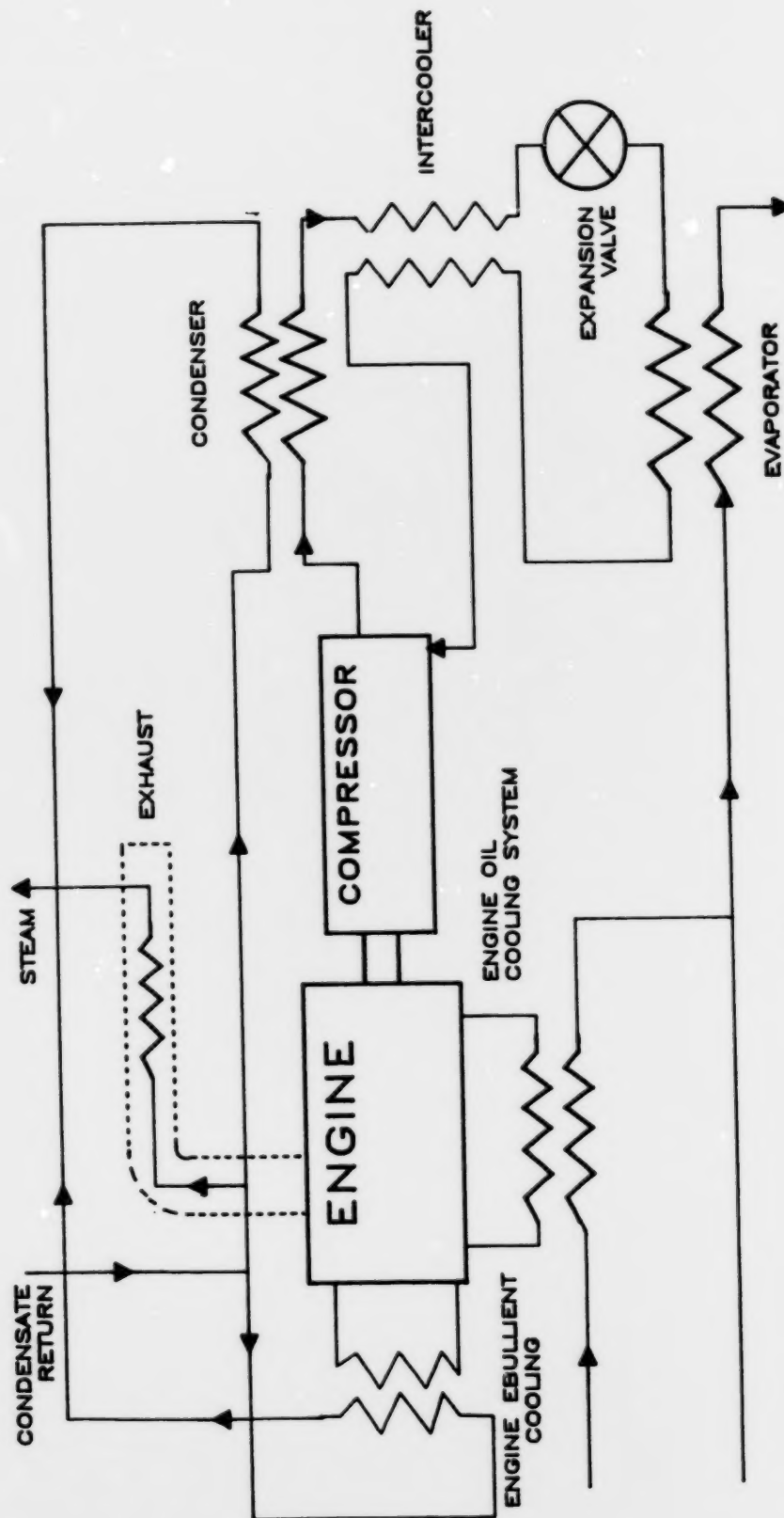


Figure #7

Schematic of a Prototype Gas Driven High Temperature Heat Pump

In 1984, the International Research and Development Company published a follow-up report based on a 2000-hour laboratory test performed on the HTCHP mentioned in the previous paragraph/14/. The test concluded that the HTCHP yielded satisfactory results when operating on R114, but further tests in an industrial environment were required. The report also outlined several candidates, such as the chemical process industry, which would be potential purchasers of such heat recovery systems.

The final working fluid to be considered here is water. For temperatures below 120°C, water is not considered as an efficient working fluid. For water, large flowrates are encountered which mean larger, more expensive compressors. Working fluids such as R114 then become more attractive due to lower flowrates and hence lower equipment costs.

For temperatures above 120°C, there are no other fluids which can be used safely. Currently, the major difficulties in designing a Very High Temperature Compression Heat Pump (VHTCHP) lies in the compressor technology available. Difficulties arise in constructing oil free compressors which handle low pressure inlet steam and deliver high pressure steam at elevated temperatures efficiently.

This problem is currently under research at the Electrical Council Research Centre, Capenhurst England by Mr. M. Bertinat/15/. Bertinat and fellow researchers are working on designing a compressor which will solve the aforementioned problems.

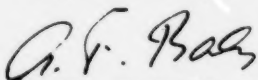
The MYCOM Corporation of Japan has developed Screw Compressors which handle inlet temperatures between 80°C and 120°C and delivery temperatures as high as 180°C. These VHTCHP are being developed for such things as heat recovery of process steam in the chemical process industries.

CONCLUSIONS AND RECOMMENDATIONS

Currently, R114 is generally recommended for use in HTCHP with condensing temperatures of 120°C or less. However, with the change in the aerosol industries, the supply of R114 may be reduced and the fluid R133a may become an economically feasible alternative due to reduced compressor costs. For condensing temperatures above 120°C, water is considered the only working fluid with adequate thermodynamic and chemical stability properties for use in HTCHP at this time.

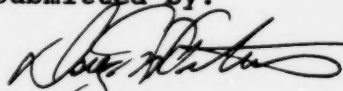
There are some areas which require further research. A more comprehensive study of the stability of R133a as a working fluid is required. Other working fluids, such as R11 and R113, should be considered when suitable dry compressors are developed and become economically attractive. Dry compressor technology should be considered for future research and development, due to the detrimental effects of some lubricants on the stability of working fluids. The results of the above research would greatly aid the advancement of HTCHP for industrial use.

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